

# Briggs–Rauscher Reaction with 1,4-Cyclohexanedione Substrate

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## *Nonlinear Dynamics / Oscillatory Reactions / Briggs–Rauscher Reaction / 1,4-Cyclohexanedione / Temperature Compensation*

A new organic substrate has been used to promote oscillations under batch conditions in the Briggs–Rauscher oscillating system. The new substrate, 1,4-cyclohexanedione (CHD), reacts with aqueous iodine *via* an enol mechanism. We discuss the effect of the initial concentrations, the temperature and chemical perturbations. In a definite range of concentrations long-lived oscillations with two significantly different frequency periods were observed. The low frequency parts are temperature-dependent while the high frequency oscillations do not show temperature dependence. The inhibitory effects of 1,4-hydroquinone and 1,4-benzoquinone on the oscillations and the kinetics of some important component reactions were studied to develop a model for the simulation of the observed oscillations.

## 1. Introduction

The Briggs–Rauscher reaction [1], referred here as BR reaction, is one of the most fascinating oscillatory reaction. This reaction is widely used as a classroom demonstration of the chemical oscillators due to the observable spectacular periodical colour changes. The “classic” BR system consists of hydrogenperoxide, iodate, Mn(II) catalyst, malonic acid as organic substrate and sulfuric acid. In the variants of the BR reaction the malonic acid is replaced with malonic acid derivatives [2], acetone [3], crotonic acid, acrylic acid, anisole and p-nitrophenol [4].

Recently BR reaction has received growing attention due to the inhibitory effects of antioxidants on the oscillatory regime [5]. These effects make the BR reaction capable to measure the antioxidant capacity of radical scavengers. Another interesting application of the BR reaction was published by Grzybowski

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and coworkers. They coupled the BR reaction with a new patterning technique (wet stamping). Large variety of novel wave phenomena, like twist-symmetry breaking and kinetic autofocusing were observed by this method [6].

Here we present a novel variant of the BR reaction with 1,4-cyclohexanedione (CHD). During the last years CHD became one of the most popular organic substrate of the Belousov–Zhabotinsky (BZ) reaction, due to its bubble-free and long-lived oscillatory behaviour [7]. The reactions of CHD with bromate and bromine were studied in detail [8]. According to the analogy between the BR and BZ reactions, we investigated CHD as a substrate of the BR reaction.

## 2. Experimental section

H<sub>2</sub>SO<sub>4</sub> (Chemolab 96%), 1,4-cyclohexanedione (Aldrich 98%), KIO<sub>3</sub> (Aldrich 99.5%), MnSO<sub>4</sub>·H<sub>2</sub>O (Reanal a.r.), Ce(NH<sub>4</sub>)<sub>4</sub>(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O (Reanal a.r.), H<sub>2</sub>O<sub>2</sub> (Reanal purris), I<sub>2</sub> (Reanal a.lt.), 1,4-hydroquinone (Fluka purris), 1,4-benzoquinone (Merck 98%) and bidistilled water were used to prepare the working solutions.

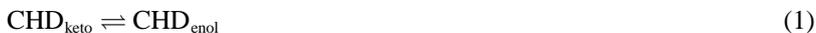
Spectra for the kinetic measurements were taken on Milton Roy 3000 and Agilent 8452 diode array spectrophotometers equipped with quartz cells (path length 1 cm, volume 2 mL). Redox potentials were monitored with a smooth Pt electrode (Radelkis) and a Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub>(sat.) reference electrode (Radiometer). Analog signals were digitized with a 12 bit AD converter (Labtech PCL-711 S) and processed on a PC. The temperature was kept at 25.0 ± 0.1 °C, and the solutions in the cell were mixed with a magnetic stirrer.

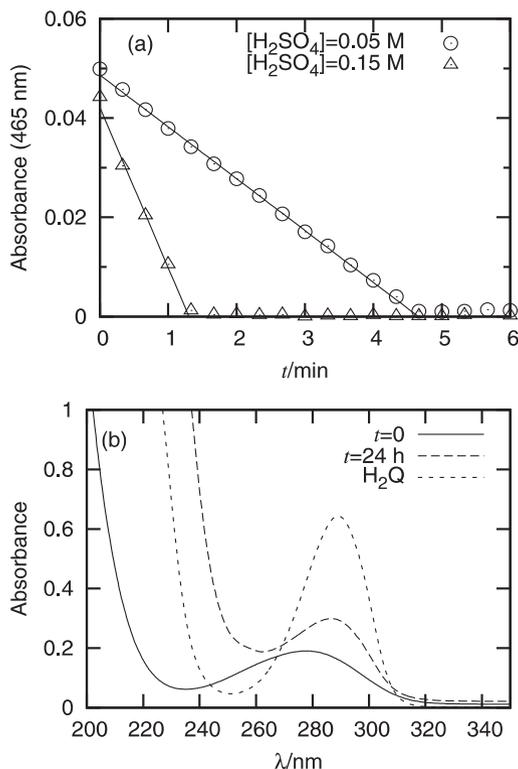
The simulations were done with the program XPPAUT [9].

## 3. Results and discussion

### 3.1 Iodination of 1,4-cyclohexanedione

The reaction between the organic substrate and iodine plays an essential role in the mechanism of the BR reaction. Noyes and Furrow pointed out, that the efficiency of the organic substrate for scavenging iodine must be in a specific range to give rise oscillations [10]. The iodination of CHD was followed at different CHD (0.03–0.09 mol/dm<sup>3</sup>), I<sub>2</sub> (2.5 × 10<sup>-4</sup>–5 × 10<sup>-4</sup>) and H<sub>2</sub>SO<sub>4</sub> (0.05–1.0 mol/dm<sup>3</sup>) concentrations. The consumption of iodine was monitored at 465 nm. The reaction is expected to proceed through an enol mechanism according to the scheme



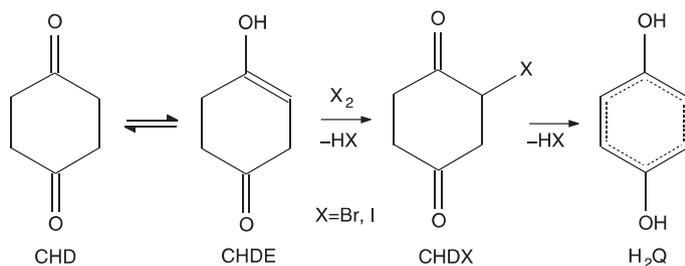


**Fig. 1.** (a) Absorbance changes during the iodination of 1,4-cyclohexanedione at 465 nm.  $[\text{CHD}]_0 = 9.0 \times 10^{-3} \text{ mol/dm}^3$ ,  $[\text{I}_2]_0 = 2.5 \times 10^{-4} \text{ mol/dm}^3$ , ( $\odot$ )  $[\text{H}_2\text{SO}_4]_0 = 0.05 \text{ mol/dm}^3$  and ( $\triangle$ )  $[\text{H}_2\text{SO}_4]_0 = 0.15 \text{ mol/dm}^3$ , (b) absorption spectra of a reacting mixture at the starting (solid line) of the reaction and after 24 hours (dashed line). Initial composition:  $[\text{CHD}]_0 = 9.0 \times 10^{-3} \text{ mol/dm}^3$ ,  $[\text{I}_2]_0 = 9.0 \times 10^{-4} \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4]_0 = 0.2 \text{ mol/dm}^3$ . The dotted line shows the spectrum of an  $2.5 \times 10^{-4} \text{ mol/dm}^3$  1,4-hydroquinone solution.

In these experiments CHD was in high excess (6–36  $\times$ ) over the iodine. The obtained absorbance vs. time curves show pseudo zero order kinetics. This observation supports that the rate determining step is the acid catalyzed enolization of CHD (Fig. 1a). From the measured data we evaluated a second order rate constant according to the rate expression

$$d[\text{I}_2]/dt = k_1[\text{CHD}][\text{H}^+]. \quad (3)$$

In the range of 0.05–1.0  $\text{mol/dm}^3$  sulfuric acid concentrations, the value of the rate constant observed is  $5.1(\pm 0.2) \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . This value is close to the other one obtained in the bromine–CHD reaction ( $2.13 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ) [8].



**Fig. 2.** Formation of H<sub>2</sub>Q in the CHD–halogen reactions. Abbreviations are: CHD ≡ 1,4-cyclohexanedione, CHDE ≡ enol form of 1,4-cyclohexanedione, CHDX ≡ halogeno-1,4-cyclohexanedione, H<sub>2</sub>Q ≡ 1,4-hydroquinone.

The ICHD is not stable, it decomposes similarly to the BrCHD (Fig. 2). The appearance of 1,4-hydroquinone (H<sub>2</sub>Q), that is the endproduct of the decomposition of ICHD, is visible on the spectrum, which was taken 24 hours later (Fig. 1b).



The rate of this reaction depends on the acidity:

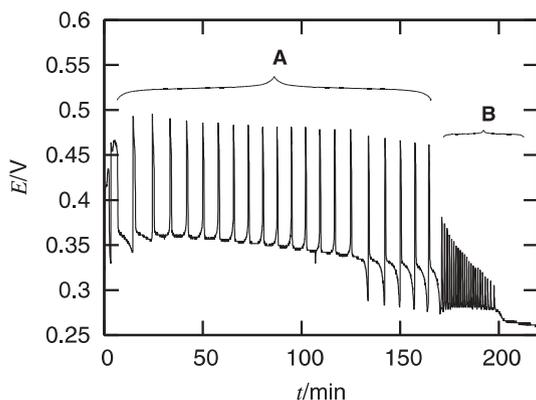
$$v = k_6[\text{ICHD}][\text{H}^+] . \quad (5)$$

The measured value of the rate constant is  $4.6(\pm 0.2) \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . There is no significant difference between the rate constants measured here for the decomposition of ICHD and previously for BrCHD ( $5.0 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ).

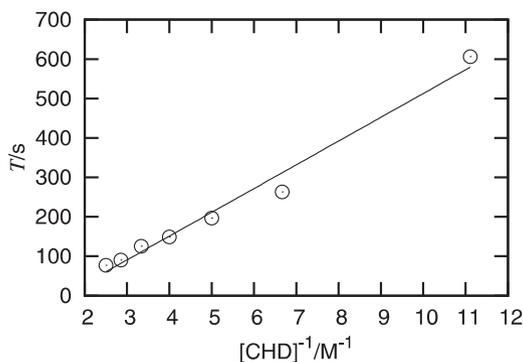
### 3.2 Oscillatory behavior

Under batch conditions oscillations appear in wide range of initial reagent-concentrations. The typical compositions of our experiments were: iodate ( $0.05\text{--}0.1 \text{ mol/dm}^3$ ) – hydrogen-peroxide ( $0.4\text{--}0.6 \text{ mol/dm}^3$ ) – Mn(II) ( $2.5 \times 10^{-4}\text{--}6.0 \times 10^{-2} \text{ mol/dm}^3$ ) – CHD ( $0.05\text{--}0.4 \text{ mol/dm}^3$ ) – H<sub>2</sub>SO<sub>4</sub> ( $0.03\text{--}0.075 \text{ mol/dm}^3$ ). The temporal evolution of the reactions can be followed by measuring the redox potential, the potential of an iodide selective electrode and the absorbance changes. In Fig. 3 we show a characteristic redox potential vs. time curve. After a relatively short induction time long lasting, low frequency oscillations (section A in Fig. 3) appear in the system. At the end of the oscillatory period the frequency suddenly switches to a significantly higher value (section B in Fig. 3). These high frequency oscillations appear in a certain range of initial Mn(II) concentrations ( $1 \times 10^{-2}\text{--}5 \times 10^{-2} \text{ mol/dm}^3$ ).

The period time of the low frequency oscillations is proportional to  $1/[\text{CHD}]$  over a wide range of the concentrations (Fig. 4). This relationship



**Fig. 3.** Oscillations in the redox potential during the iodate–hydrogen-peroxide–Mn(II)–CHD reaction. After a long lasting, low frequency oscillatory period (A) suddenly high frequency oscillations (B) appear. Initial concentrations:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{CHD}] = 0.09 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ .

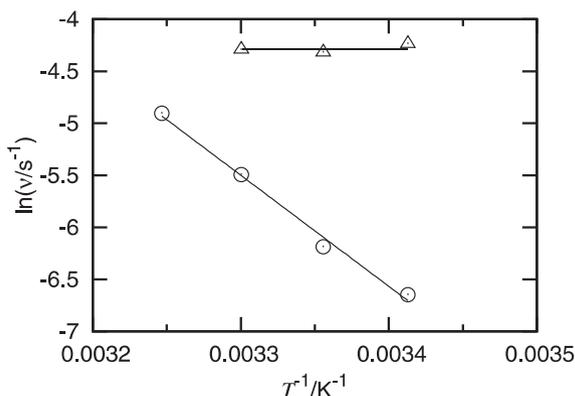


**Fig. 4.** Effect of changing the initial concentration of CHD on the period time of the oscillations. Initial concentrations:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ .

supports that the oscillation period is mainly effected by the iodine consumption. This is in agreement with earlier observations with other substrates like acetone [3], malonic acid and derivatives of malonic acid [2].

### 3.3 Effect of the temperature

To characterize the temperature dependence of the oscillatory reactions Kőrös suggested to use the Arrhenius equation for calculating the “apparent activation energy”, by plotting the logarithm of the frequency as a function of



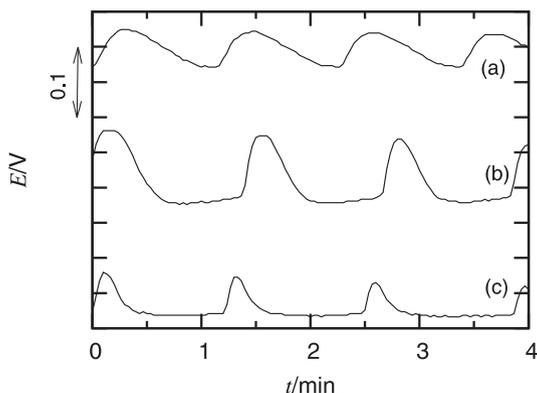
**Fig. 5.** The frequency of the low frequency oscillations ( $\odot$ ) and the high frequency oscillations ( $\triangle$ ) as a function of  $1/T$ . Initial concentrations:  $[KIO_3] = 0.083 \text{ mol/dm}^3$ ,  $[MnSO_4] = 0.00815 \text{ mol/dm}^3$ ,  $[H_2SO_4] = 0.053 \text{ mol/dm}^3$ ,  $[CHD] = 0.09 \text{ mol/dm}^3$ ,  $[H_2O_2] = 0.5 \text{ mol/dm}^3$ .

$1/T$  [11]. Here we obtained  $89 \pm 5 \text{ kJ/mol}$  for the long lasting, low frequency oscillations (Fig. 5). This value is higher than the value of the activation energy measured in the “classical” Briggs–Rauscher reaction with malonic acid ( $68 \pm 2 \text{ kJ/mol}$ ) [5] or with benzylmalonic acid substrate ( $57.8 \text{ kJ/mol}$ ) [12]. Cervellati and coworkers obtained such high activation energy after adding radical scavengers (antioxidants), diphenol derivatives into the “classical” BR reaction. They assumed that in this phase of the reaction the substrate is one of the degradation product of the antioxidants, instead of the malonic acid.

However, the activation energy of the high frequency oscillations (section B on Fig. 3) seems to be zero within the experimental error (Fig. 5). Temperature-independent period length or temperature compensation is an essential feature of some biological rhythms. Rábai and coworkers studied this phenomenon in different oscillatory reactions [13]. Recently, they observed temperature compensation in the iodate–hydrogen–peroxide reaction, a subsystem of the BR reaction [14]. They suggested to use the  $Q_{10}$  value to characterize the temperature dependence of the oscillatory reactions, which describes the relative change in the period length when the temperature is increased by  $10^\circ\text{C}$ . It is defined as follows:

$$Q_{10} = (P_1/P_2)^{10/(T_2-T_1)}, \quad (6)$$

where  $P_1$  and  $P_2$  are the period length in seconds at  $T_1$  and  $T_2$  absolute temperatures, respectively. In the low frequency part we evaluated  $Q_{10} = 3.4$ , while in the high frequency part  $Q_{10}$  appears close to 1.0 ( $Q_{10} = 0.94$ ). The latter value indicates temperature compensation. In Fig. 6 we show the redox poten-



**Fig. 6.** High frequency oscillations at (a) 20 °C, (b) 25 °C and (c) 30 °C. Initial concentrations:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{CHD}] = 0.09 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ .

tial vs. time curves at three different temperatures. It is clearly visible that there is no significant change in the period-time. Note that above 35 °C these high frequency oscillations disappear.

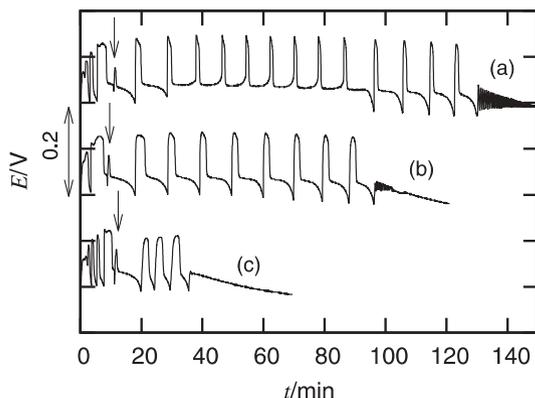
### 3.4 Effect of 1,4-hydroquinone and 1,4-benzoquinone

As we discussed previously the decomposition of ICHD produces slowly  $\text{H}_2\text{Q}$ , which is known to be an inhibitor of the oscillations in the BR reaction [5]. Cervelatti and coworkers found out that adding antioxidants (e.g. diphenols) to the oscillating BR mixture (with malonic acid substrate) stops the oscillations immediately. However, after a definite inhibition time, depending on the antioxidant concentration, oscillations restart. They assumed that the inhibitory effects are due to the  $\text{HOO}\cdot$  scavenging action of the diphenols and the quinones.

The effect of  $\text{H}_2\text{Q}$  on the iodate–hydrogen–peroxide–Mn(II)–CHD reaction is shown on Fig. 7. In this system oscillations are not terminated below a critical concentration of  $\text{H}_2\text{Q}$ , that is  $5 \times 10^{-4} \text{ mol/dm}^3$ . The main effect is the total oscillatory period-shortening. Above this limit oscillations are stopped, and we did not observed any subsequent regeneration of oscillations like in the “classical” BR reaction. In a typical BR mixture, the lifetime of  $\text{H}_2\text{Q}$  is short, due to its fast reactions with iodate and iodine [5]. However, the time scale of the effect of adding  $\text{H}_2\text{Q}$  is quite long. Seemingly  $\text{H}_2\text{Q}$  affects the oscillatory behaviour after hours of the addition (Fig. 7).

Cervelatti and coworkers assumed that 1,4-benzoquinone (Q), which is the oxidation product of  $\text{H}_2\text{Q}$ , has scavenging effect according to reaction (7):





**Fig. 7.** Effect of 1,4-hydroquinone on the oscillatory behaviour. The arrows indicate the injection-time of 1,4-hydroquinone into the oscillatory system. Initial concentrations:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{CHD}] = 0.09 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ , (a)  $[\text{H}_2\text{Q}] = 1.0 \times 10^{-4} \text{ mol/dm}^3$ , (b)  $[\text{H}_2\text{Q}] = 1.5 \times 10^{-4} \text{ mol/dm}^3$  and (c)  $[\text{H}_2\text{Q}] = 2.5 \times 10^{-4} \text{ mol/dm}^3$ .

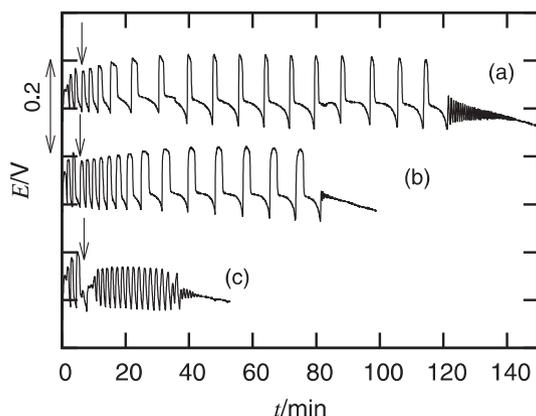
It means that both  $\text{H}_2\text{Q}$  and  $\text{Q}$  act as an inhibitor in the system. The effect of  $\text{Q}$  on the oscillations is presented in Fig. 8. Similar to  $\text{H}_2\text{Q}$ ,  $\text{Q}$  shortens the length of the oscillatory period and stops the oscillations above a certain concentration limit. Contrary to  $\text{H}_2\text{Q}$ ,  $\text{Q}$  increases the oscillations frequency significantly. We think that, besides the reaction of  $\text{Q}$  with  $\text{HOO}\cdot$  radicals, the reaction of  $\text{Q}$  with iodide ions must be taken into account. We have tested spectrophotometrically that  $\text{Q}$  can oxidize iodide ions to iodine at  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ .



This reaction may have important role in the mechanism, since iodine and iodide are key intermediates of the BR reaction. In the unperturbed system, before termination of the oscillations, the frequency suddenly increases (Fig. 3). We assume that slow production of  $\text{H}_2\text{Q}$  and  $\text{Q}$  from  $\text{CHD}$  leads to this phenomenon.

### 3.5 Simulations

For the simulations we used an extended version of the FCA model of the BR reaction [4,5]. The mechanism and the rate laws are presented in Tables 1 and 2. This model contains 13 variables ( $\text{HOI}$ ,  $\text{I}^-$ ,  $\text{I}_2$ ,  $\text{HOIO}$ ,  $\text{IO}_3^-$ ,  $\text{IO}_2\cdot$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HOO}\cdot$ ,  $\text{CHD}$ ,  $\text{CHDE}$ ,  $\text{ICHD}$ ,  $\text{H}_2\text{Q}$ ,  $\text{Q}$ ). The concentrations of  $\text{Mn(II)}$  and  $\text{H}^+$  are parameters. The role of manganese ion in the mechanism of the BR reaction is not understood completely [4]. We used the rate constant reported by Furrow *et al.* [4,5]. The reaction of  $\text{CHD}$  and iodine is studied



**Fig. 8.** Effect of 1,4-benzoquinone on the oscillatory behaviour. The arrows indicate the injection-time of 1,4-benzoquinone into the oscillatory system. Initial concentrations:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{CHD}] = 0.09 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ , (a)  $[\text{Q}] = 1.0 \times 10^{-4} \text{ mol/dm}^3$ , (b)  $[\text{Q}] = 1.77 \times 10^{-4} \text{ mol/dm}^3$  and (c)  $[\text{Q}] = 2.17 \times 10^{-4} \text{ mol/dm}^3$ .

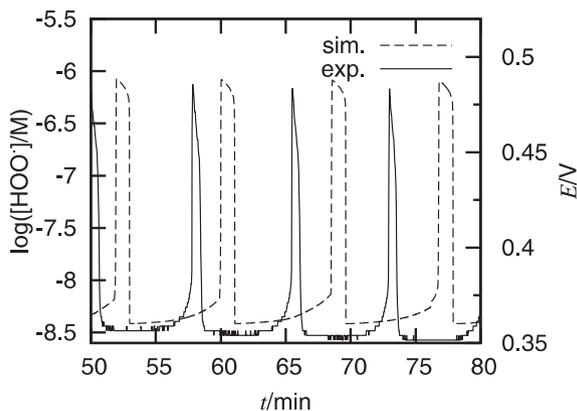
**Table 1.** Extended FCA model.

step	
R1	$\text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$
R1r	$\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{I}^- + \text{H}^+$
R2	$\text{I}^- + \text{HOIO} + \text{H}^+ \rightarrow 2\text{HOI}$
R3	$\text{I}^- + \text{IO}_3^- + 2\text{H}^+ \rightarrow \text{HOI} + \text{HOIO}$
R4	$2\text{IO}_2\cdot + \text{H}_2\text{O} \rightarrow \text{HOIO} + \text{IO}_3^- + \text{H}^+$
R5	$\text{HOIO} + 2\text{H}_2\text{O}_2 + \text{Mn(II)} \rightarrow$ $2\text{HOO}\cdot + \text{HOI} + \text{Mn(II)} + \text{H}_2\text{O}$
R6	$\text{H}^+ + \text{IO}_3^- + \text{HOO}\cdot \rightarrow \text{IO}_2\cdot + \text{H}_2\text{O} + \text{O}_2$
R7	$\text{IO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{HOO}\cdot$
R8	$\text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{O}_2 + \text{H}^+ + \text{H}_2\text{O}$
R9	$2\text{HOO}\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
R10	$\text{CHD} \rightleftharpoons \text{CHDE}$
R11	$\text{CHDE} + \text{I}_2 \rightarrow \text{ICHD}$
R12	$\text{ICHD} \rightarrow \text{H}_2\text{Q} + \text{I}^- + \text{H}^+$
R13	$2\text{IO}_3^- + 5\text{H}_2\text{Q} + 2\text{H}^+ \rightarrow \text{I}_2 + 5\text{Q} + 6\text{H}_2\text{O}$
R14	$\text{H}_2\text{Q} + \text{I}_2 \rightarrow \text{Q} + 2\text{I}^- + 2\text{H}^+$

here. The backward rate constant of the reaction R10 is calculated by using the enolization equilibrium constant reported by Keeffe and coworkers [15]. The reaction of the enol form with halogens are reported as diffusion controlled reactions [16], but the FCA model does not show oscillations with

**Table 2.** Rate laws used for simulation.

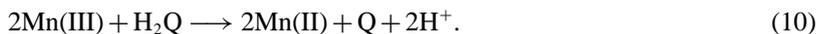
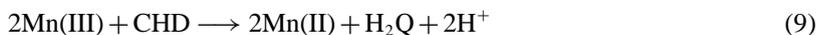
step	rate law	ref.
R1	$3.67 \times 10^9 [\text{HOI}][\text{I}^-]$	[4]
R1r	$1.98 \times 10^{-3} [\text{I}_2]/[\text{H}^+]$	[17]
R2	$5 \times 10^9 [\text{I}^-][\text{HOIO}]$	[4]
R3	$1430 [\text{I}^-][\text{IO}_3^-][\text{H}^+]^2$	[18]
R4	$5 \times 10^9 [\text{IO}_2]^2$	[4]
R5	$3.1 \times 10^4 [\text{HOIO}][\text{H}_2\text{O}_2][\text{Mn(II)}]$	[4]
R6	$1.3 \times 10^4 [\text{H}^+][\text{IO}_3^-][\text{HOO}\cdot]$	[4]
R7	$20 [\text{IO}_2][\text{H}_2\text{O}_2]$	[4]
R8	$5 [\text{HOI}][\text{H}_2\text{O}_2]$	[2]
R9	$7.5 \times 10^5 [\text{HOO}\cdot]^2$	[19]
R10	$5.1 \times 10^{-4} [\text{CHD}] - (5.1 \times 10^{-4}/4.07 \times 10^{-7}) [\text{CHDE}]$	this work
R11	$7 \times 10^5 [\text{CHDE}][\text{I}_2]$	this work
R12	$4.6 \times 10^{-5} [\text{ICHD}][\text{H}^+]$	this work
R13	$120 [\text{IO}_3^-][\text{H}_2\text{Q}][\text{H}^+]$	[5]
R14	$10 [\text{H}_2\text{Q}][\text{I}_2]$	[5]



**Fig. 9.** Comparison of the simulated and the experimentally observed oscillations. Initial concentrations in the experiment:  $[\text{KIO}_3] = 0.083 \text{ mol/dm}^3$ ,  $[\text{MnSO}_4] = 0.00815 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{SO}_4] = 0.053 \text{ mol/dm}^3$ ,  $[\text{CHD}] = 0.09 \text{ mol/dm}^3$ ,  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/dm}^3$ . In the simulation the initial concentrations of  $\text{KIO}_3$ ,  $\text{CHD}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Mn(II)}$  are the same like in the experiment and for  $[\text{H}^+]$  we used  $0.058 \text{ mol/dm}^3$ .

$k_{11} = 2.8 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . We adjusted  $k_{11}$  to get the appropriate period time. The obtained model is capable to simulate the long lasting low frequency oscillations (Fig. 9).

The simulation of the high frequency oscillations appear at the end of the oscillatory period requires more kinetic informations. We assume that Q plays an essential role in this part of the reaction. It can react with the key intermediates,  $\text{HOO}\cdot$  and iodide ion, of the BR reaction. We discussed here that Q forms as the oxidation product of CHD by iodine. However, the oxidation of CHD by Mn(III) produces Q also [7]:



Since the high frequency oscillations appear in a definite range of the initial Mn(II) concentration, these reactions must be taken into account in the simulations. The extension of the model with the reactions related to the Q is in progress.

## 4. Conclusion

Here we present a novel variant of the BR reaction. The BR reaction with CHD shows long lasting oscillations under batch condition in wide range of the initial reagent-concentrations. Remarkably a high frequency, temperature compensated oscillations appear at the end of oscillatory period. The iodine–CHD reaction was found to be similar to the bromine–CHD reaction, the primary products (BrCHD and ICHD) in both cases are unstable in acidic solutions. The halogeno derivatives of CHD decompose to  $\text{H}_2\text{Q}$ . The experiments presented here support that the reactions of the oxidation products of CHD,  $\text{H}_2\text{Q}$  and Q have a significant effect on the observed behavior.

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